

# Supercritical CO<sub>2</sub> Extraction of Compounds with Antioxidant Activity from Fruits and Vegetables Waste -A Review

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## Abstract

The Supercritical Fluid Extraction (SCFE) is gaining increasing interest in last decades because of its suitability for extraction and purification of compounds having low volatility or which are susceptible to thermal degradation. This review provides an updated overview on the applications of SCFE in recovery of bioactive compounds from fruits and vegetable wastes/by-products emphasizing the effects of various process and role process parameters on the extraction yield of these compounds. A comprehensive review of the widely used mathematical models to describe the SCFE process is also presented. It is anticipated that this article will provide useful information to researchers pursuing work on SCFE behavior of biological materials and their byproducts as well as modeling of the process.

## Keywords

*Supercritical Fluid Extraction; Antioxidants; Phase Equilibrium; Mass Transfer; Modeling*

## Introduction

Globally about 5.6 million tonnes of fruits and vegetables are annually wasted due to lack of storage and processing facilities. These huge amounts of wastes are generally disposed of by dumping on the outskirts of cities. Extraction of valuable bioactive compounds from waste products generated by food industries is an important means of producing value added products, which is considered to have a beneficial effect on health. Natural food additives are gaining more and more importance than synthetic compounds due to their extensive use in food, cosmetics and pharmaceuticals industries.

Fruits and vegetables are rich in a group of natural compounds known as polyphenols. These plant-based compounds have strong antioxidant activity that protect against oxidation, or cellular damage caused

by free radicals that are harmful to the body. The antioxidants molecules provide good health to the immunity system of our body and are effective in helping to prevent diseases. Vitamin E, vitamin C,  $\beta$ -carotene, selenium and zinc are common antioxidants found in fruits and vegetables. The antioxidative phytochemicals in grains, vegetables, fruits and medicinal plants have received increasing attention for their potential role in preventing human diseases such as cancer, coronary heart disease and even altitude sickness. Apricots, carrots, pumpkin and sweet potatoes are rich in carotene that is a healing agent and works against cancer. This valuable  $\beta$ -carotene is also found in asparagus, beets, broccoli, mangoes, turnip, peaches, spinach, tomatoes, and watermelon. Ripe tomatoes are the most abundant source of lycopene, which helps in minimizing the risk of cardiovascular ailments and different forms of cancers.

However, only a few byproduct derived antioxidants have been developed successfully from the vast quantities of food wastes produced by the food processing industry. Recent research has revealed that fruit and vegetable wastes, such as grape peels, banana peel, orange peel, orange pomace, apricot pomace, raspberry waste potentially possess antioxidant properties.

The extraction and purification processes of these bioactive compounds are essential as they can be used in the preparation of dietary supplements, nutraceuticals, and functional food ingredients, and food additives, pharmaceutical and cosmetic products. Various extraction processes have been in use for the extraction of organic compounds from complex solid samples; including soxhlet extraction, microwave extraction, sonication & pressurized solvent extraction.

Conventional separation techniques such as solvent extraction and distillation have the drawback of leaving trace amounts of organic solvents or to cause thermal degradation. They are time consuming and need large amounts of solvents. Supercritical fluid extraction using carbon dioxide is a promising alternative for the extraction of value added products since mild temperature is used which allows the extraction of thermally labile or easily oxidized compounds.

In Supercritical fluid, the physicochemical properties of a given fluid, such as density, diffusivity, dielectric constant and viscosity can be easily controlled by changing the pressure or the temperature without ever crossing phase boundaries. Supercritical fluids have liquid like densities and higher diffusion coefficient and low surface tension resulting in easy penetration of the supercritical solvent into the porous structure of the solid matrix to release the solute. The critical point of carbon dioxide (CO<sub>2</sub>) is at 31.06 °C and 7.386 MPa. CO<sub>2</sub> is the solvent of choice for use in supercritical fluid extraction because it is, "Generally regarded as safe (GRAS), non-toxic, non-flammable, inexpensive and its critical temperature and pressure are relatively low which helps in preventing thermal degradation of food components being extracted. The problem with most of the fluids besides CO<sub>2</sub> is that they cannot be obtained in pure form and they are difficult to handle. The advantages of SCFE are:

1. Supercritical fluids have a higher diffusion coefficient and lower viscosity than liquids which helps to a more favorable mass transfer.
2. Absence of surface tension allows for their rapid penetration into the pores of solid matrices, which enhances the extraction efficiencies.
3. The extraction conditions may be manipulated by varying temperature and pressure affecting the solubility of the various components in the supercritical fluid.
4. SCFE does not leave a chemical residue, considered as an environment friendly separation process.
5. Supercritical fluid extractions use carbon dioxide gas, which can be recycled and used again as part of the unit operation.

CO<sub>2</sub> dissolves non-polar or slightly polar compounds and therefore not a very good solvent for high molecular weight and polar compounds. To increase

the solubility of such compounds in supercritical carbon dioxide, small volumes (ranging from 0 to 20 mol %) of modifiers (water, methanol, ethanol, hexane, dichloromethane etc.) may be added that are generally polar or non-polar cosolvents which increase the solvating power by interacting with solute.

### Extraction and Characterization of Functional Compounds

Fruits and vegetables contain different kinds of phytochemicals such as vitamins, carotenoids and polyphenols, which significantly affects their taste, color and nutritive values. The waste and by-products of fruits and vegetables are abundant source of antioxidant polyphenols and therefore the recycling of the byproducts as a source of polyphenols can be of considerable economic benefit to food processors. In addition to their potential health benefit, natural extracts high in antioxidant activity can be added to food products to preserve their colour and flavour and hence improve their shelflife.

### *Polyphenolic Compounds*

Natural phenols have excellent properties as food preservatives and play an important role in the prevention of cardiovascular illnesses, certain kinds of cancer, diabetes, brain dysfunction or other conditions associated with the aging process. Besides the use of polyphenols as natural colorants or preservatives, for foods, they are also being used in the production of paints, paper, and cosmetic. Citrus by-products such as orange pomace, orange peel, grape peel, grape skin, are a good source of phenolic compounds. According to the number of phenol rings, polyphenols are categorized into flavonoids, phenolic acids, tannins (hydrolysable and condensed), stilbenes and lignans. Flavonoids can be further classified into anthocyanins, flavones, isoflavones, flavanones, flavonols and flavanols. Phenolic acids are a type of organic compounds and constitute about one-third of the dietary phenol present in plants in free and bound forms. Tannin is a bitter plant polyphenolic compound, the modification of which with time plays an important role in the ripening of fruit. Stilbene derivatives (stilbenoids) are present naturally in plants and found in low quantities in the human diet. The main representative is resveratrol which exists in both cis and Trans isomeric forms, mostly in glycosylated forms. Lignans are produced by oxidative dimerisation of two phenylpropane units that are mostly present in nature in the free form.

TABLE 4 OPERATING CONDITIONS FOR THE EXTRACTION, RECOVERY AND CHARACTERIZATION OF EXTRACT FROM FOOD WASTES USING SUPERCRITICAL EXTRACTION

Sample	Parameters evaluated						Analyte	Reference
	Temperature (K)	Pressure (MPa)	Time (h)	Flow rate (g/min)	Co-solvent (%)	Particle size (mm)		
Red pepper by-products	318.15 & 333.15	20,24,30	1.5-2	33.33	Ethanol	0.2,0.5,1.25	Vitamin E and Vitamin A	Hualde et al.
Grape seed	313.15	16,18,20	---	1.02×10 <sup>9</sup>	---	0.75	Grape seed oil	Claudia et al.
Banana peel	313.15 to 323.15	10-30	0- 4	5.0	---	0.428	Essential oil	Comim et al.
Elderberry Pomace	313	21	1.6	---	CO <sub>2</sub> (0-90)/ethanol(0.5-100)/H <sub>2</sub> O( 0-95)	---	Anthocyanin	Seabra et al.
Orange pomace	313.15 and 323.15	10 to 30	5	17	Ethanol (2, 5, 8)	0.597	Orange oil	Benelli et al.
Grape peel	310.15, 313.15, 316.15 & 319.15	13.7, 14.7, 15.7 and 16.7	0.5	---	Ethanol (5,6,7 and 8)	---	Phenolic compounds, antioxidants & anthocyanins	Ghafoor et al.
Guava seed	313.15, 323.15, 333.15	10,20,30	2	---	Ethyl acetate, Ethanol (10)	---	Phenolic fractions	Henry et al.
Peach kernels	300, 310 and 320	10, 20 and 30	2.5	8.3 ± 0.8	Ethanol (2 and 5)	---	Peach almond oil	Natalia et al.
Grape pomace	308 and 328	10 and 40	3	0.8	Ethanol (5)	---	Resveratrol	Casas et al.
Tomato skin	310-400	20-40	1.5	1-2	---	---	Lycopene	Chun et al.
Tomato skin	318.15, 333.15,348.15	25, 30, and 35	---	3500	Ethanol, water, and canola oil (5, 10, & 15)	1	Lycopene	Shi et al.
Pumpkin	308.15-348.15	0.15,0.02 ,0.024,0.03,0.034	0.5,1,1.5,2	250	---	0.5	Pumpkin seed oil	Mitra et al.
Tomato waste	313.15, 333.15, 353.15	20 and 30	5.8	0.26,0.59 and 1.05	---	0.15, 0.36 & 0.72	Trans-lycopene	Nobre et al.
Peach seed	313.15 and 324.15	15.0 and 19.8	8	0.79 and 2.37	Ethanol (2.5 & 5.0 mol%)	0.25 to 0.35	Peach seed oil	Yolanda et al.
Pomegranate seed	306.35,313.15,323.15,333.15,339.95	13.2,20,30,40,46.8	2	6.6,10,15 ,20, 23.4	---	---	Pomegranate seed oil	Guangmin et al.
Tomato skin	313.15 and 343.15	25 and 45	0.17-0.33	3500	Ethanol (5 and 15)	0.5-1	Lycopene	Lamin et al.
Grape pomace	308.15 and 323.15	8 and 35	1	3200	Ethanol (0 and 8)	---	Phenolic	Pinelo et al.

							Antioxidants	
Grape seed	310 and 353.15	25	7	---	---	1.125, 0.638, 0.363	$\alpha$ -tocopherol-enriched oil	Bravi et al.
Apple and peach pomaces	313.15–333.15	20–60	0.17–0.67	2	Ethanol (14–20)	0.638	Polyphenols	Adil et al.
Tomato pomace	313.15, 333.15, 353.15	30,38,46	---	---	---	0.3, 0.4, 0.6	Carotenoids, tocopherols, fatty acids and sitosterols	Vagi et al.
Tomato skin	373	40	---	2.5	---	---	Lycopene	Topal et al.
Wine industry waste (red grape pomace)	318.15	10,15,25	---	18.3	Methanol (5)	---	Phenolic antioxidants	Louli et al.
Apricot pomace	313–333	30.4–50.7	0–2.67	0.5–2.0	Dimethoxypropane	0.07–0.6	Carotenoids	Sanal et al.
Apricot pomace	316–350	13.3–47.3	1.5	1	Ethanol (2–28)	0.07–0.6	$\beta$ -carotene	Sanal et al.
Sweet potato waste powder	310,320, 350	10–35	2	5X10 <sup>3</sup>	---	0.18	$\beta$ -carotene and $\alpha$ -tocopherol	Okuno et al.
Cherry seeds	313–333	18–22	---	---	---	1.25–2.25	Cherry seed oil	Gabriela et al.
Grape skin	313.15	15	0.25	2	Ethanol (7.5)	---	Resveratrol	Marti et al.
Orange peel	313	20	7	16.7 and 333.3	---	---	Essential oil	Berna et al.
Orange peel	293 to 323	8–28	---	8.3 to 58.3	---	0.1 to 10	limonene & linalool	Mira et al.
Grape seed	313.15	28	3	500	---	---	Grape seed oil	Aleksovski et al.

### Carotenoids Compounds

Carotenoids represent one of the most widespread groups of naturally occurring pigments found in fruits and vegetables and serve as powerful antioxidant and precursors of vitamin A. These compounds are largely responsible for red, yellow, and orange color of fruits and vegetables. Important functions to these compounds include anticancer activity, regulation of the immune system, free radical inactivation and fat peroxidation inhibition. They are categorised into two classes, xanthophylls (lutein and zeaxanthin) and unoxxygenated carotenoids known as carotenes ( $\alpha$ -carotene,  $\beta$ -carotene and lycopene). It is reported that the peel of tomato is richer in lycopene than the pulp.

According to Wandawi et al., carotenoids are mainly found in skin of the fruit; the amounts of lycopene and  $\beta$ -carotene are higher in skin and at least five times higher in tomato waste than in other tomato products (Table 2). It has also been found that apricot pomace, banana peel are also a source of  $\beta$ -carotene. Table 3 shows the  $\alpha$ -carotene and  $\beta$ -carotene content of various raw materials.

Several researchers have successfully extracted many functional compounds/ bioactive components by supercritical carbon dioxide extraction and have established the environmental soundness of technology and complimentary safe solvent for extracting food grade bioactive components from

industrial food wastes. Parameters used for the extraction, recovery, and characterization of bioactive components from fruits and vegetables waste using supercritical extraction are summarized in Table 4

TABLE 2 LYCOPENE CONTENT OF VARIOUS TOMATOES AND TOMATO BY PRODUCTS

Material	Carotenoids		Reference
	$\alpha$ -carotene ( $\mu\text{g/g}$ )	$\beta$ -carotene ( $\mu\text{g/g}$ )	
Freeze dried carrots	16.27	33.39	Marleny et al.
Crude carrot oil	137.8-330.3	171.7-386.6	Mei and Temelli
Tomato waste	---	15	Vagi et al.
Apricot pomace	---	88	Sanal et al.
Tomato juice	---	0.4	Thais et al.

TABLE 3 A-CAROTENE AND B-CAROTENE CONTENT OF VARIOUS RAW MATERIALS

Material	Lycopene yield (mg/100g)	Optimum conditions (SCFE)	References
Ripe tomato skins	64.4	80°C/4000psi	Enzo et al.
Tomato seeds and skin	0.719	86°C, 34.47 MPa, 2.5 mL/min	Rozzi et al.
Tomato skin	118	40 MPa, 373 K, and 2.5 mL/min	Topal et al.
Tomato pomace	31.40	460 bar and 80 °C	Vagi et al.
Dried tomato pomace	28.64	57°C/40 Mpa/1.8 hr	Wen et al.
Tomato skin	3.1	100°C, 40 MPa and 1.5 mL/min	Chun et al.

#### Effect of Process and Material Parameters on SCFE Yield

Temperature, pressure, solvent flow rate and type of solvent are important process parameters while origin of the plant material, chemical composition and particle size of the material, different types of tissues (leaves, stems, seeds, etc.) and other variables, like pretreatment and storage conditions also affect yield and the composition of the extract in SCFE. Optimization of the process and material parameters are important to provide maximum yields with highest quality and making the final product suitable for use in foods, cosmetic or pharmaceutical industries.

#### Effect of Temperature on SCFE

The effect of temperature is more confound as there is a competing solubility effect caused by the increase in vapor pressure and the decrease in density upon the increase of temperature. The density of CO<sub>2</sub> at constant pressure is reduced with increasing temperature and leading to reduction of fluid solvent power. In a work done by Natalia et al. it was observed that at 100 bar, raising extraction temperature decreased the yield of peach almond oil, due to the reduction in solvent density while at higher pressures (above 200 bar), the increase in the extracting temperature provided an increase in the yield, despite the reduction in solvent density. These opposite effects on the overall extraction yields were responsible for the inversion of the yield isotherms. Therefore, considering the crossover characteristic they suggested that, at pressures below the crossover pressure, the density effect was dominant, while above this condition the solute vapor pressure was the leading mechanism affecting the extraction process. With the increase in temperature, there is improvement in the mass transfer and the extraction yield. The increase in temperature causes the enhancement of the vapor pressure of the extractable compounds which is more significant than the reduction in the solvent density, increasing consequently the overall extraction yield. Thus, the tendency of the compounds to be extracted is increased as they can pass to the supercritical fluid phase.

Most of the carotenoids occur naturally as trans-isomer in plants. However during processing of food, cis-isomers may increase due to the isomerization of the trans-isomer of carotenoids. Factors like heat, light, and structural differences affect the isomerization of carotenoids in foods. All-trans- $\beta$ -carotene is very unstable and can be easily isomerized into cis-isomers, when exposed to heat and light. According to Konar, in SCFE, extraction under low pressure and temperature conditions can inhibit trans-cis isomerization but the products should be protected against heat and oxygen. Solubility rises depending on both pressure and temperature and it has a significant role in efficiency of extraction. In the extraction of lycopene, 60- 70 °C was reported to be the optimum temperature while significant thermal degradation was observed at 80°C. The solubility of lycopene in SC-CO<sub>2</sub> is at higher levels at low temperatures. However, extraction of lycopene from tomatoes by supercritical CO<sub>2</sub> fluid results in less isomerization and decomposition. Increasing temperatures significantly

increased degradation, which occurs mainly through oxidation without isomerization in the range 25–50 °C and with isomerization at temperatures in the range 75–150 °C. In a study conducted by Nobre et al., there was slight increase in the recovery of the carotenoid when the temperature increased from 40 to 60 °C and remained almost the same with further rise of the temperature to 80 °C. That increase is possibly due to some isomerization occurred at the higher temperature. Many authors have reported extraction temperatures above which isomerization of carotenoids occurs. Taking this into account it can be concluded that SCFE under mild working conditions can avoid trans to cis isomerization.

#### *Effect of Pressure on SCFE*

An increase in pressure at constant temperature, and increased density of the solvent alter the solute solubility and the vapor pressure of the solute decreases. At elevated pressure, the magnitude of such a density change becomes smaller and the solute vapor pressure change becomes more effective which can easily overcome the effect of solvent density change on the extraction rate. A higher recovery of volatile fractions and a lower recovery of non-volatile fractions are obtained with increasing pressure in the process. Therefore, the composition of the extract can be controlled by regulating pressure. At high pressure, there is an increase in the extraction yield with temperature rise which is due to the enhancement in solute vapor pressure and the reduction of solvent density. Similar results have been obtained in studies conducted by. However, at low pressures, the decrease in solvent power due to reduction in solvent density is the leading mechanisms. These opposite effects cause the inversion of the extraction yield isotherms, a phenomenon known as crossover yield isotherms or retrograde phenomenon. Benelli et al. observed the similar behavior in the extraction of bioactive extracts from orange pomace which shows that the crossover phenomenon for the orange pomace yield isotherms was detected between 140 and 150 bar.

#### *Effect of Particle Size on SCFE*

The extraction yield increases with decreasing particle size, as grinding before extraction not only increase the interfacial area but also releases solutes by destroying inner structures of the particles, which results in higher extraction rate. The intraparticle diffusion resistance is smaller for smaller particle size due to the shorter diffusion path. An increasing amount of the

extract versus particle size has been noticed and in their studies who concluded that cellular structures should be broken to get a complete extraction of substances.

#### *Effect of Extraction Time on SCFE*

Extraction time in SCFE is one of the very important variables as the efficiency of the recovery yield can be enhanced if the contact of the supercritical solvent with the feed material is maximized. Analysis of the process is performed considering the overall extraction curves (yield vs extraction time) which gives information regarding time required for extraction process to obtain an economical advantageous process. The curve presents three stages: a constant extraction rate period (CER), where the solute is easily transferred from solid to fluid phase, a falling extraction rate period (FER), and finally, the diffusion controlled rate period (DC). Minimum cost of manufacturing is obtained in extraction times close to the end of the constant extraction rate region (CER), in which the lowest time and highest rates of recovery of target compounds are observed (Rosa and Meireles, 2005a). According to Adil et al., the total phenolic content and antiradical efficiencies of the extracts from apple and peach pomace increased with extraction time from 10 to 40 mins, which remained constant at around 40 min. Mandana *et al.* reported a similar effect of dynamic time on the extraction yield of spearmint (*Mentha spicata* L.) leaves in SC-CO<sub>2</sub> by applying three different dynamic times (30, 60 and 90 min). It was observed that at 100 bar, the extraction yield increased with time (until 90 min). Extraction time also depends upon the type of material, solute concentrations in the matrix, CO<sub>2</sub> flow rate and operation conditions. In a work done by Sanal et al., longer extraction time resulted lesser recovery of the  $\beta$ -carotene, possibly due to degradation.

#### *Effect of Flow Rate on SCFE*

The mass transfer process is controlled by the equilibrium between the solid and the fluid phase. At the beginning of the extraction, when the flow rate is increased the recovery of extract is faster and at the end of extraction the recovery is almost the same at the lowest flow-rates. According to Doker et al., on increasing of the flow rate the thickness of the film layer around the solid particles reduces and mass transfer resistance surrounding the solid particle becomes small which results in increase in extraction yield with increase of the flow rate. Similar effect was

observed by Guangmin et al. in his studies that CO<sub>2</sub> flow rate had a positive and significant effect on the pomegranate seed oil yield. The fact that the highest flow-rate results in the lowest recovery could be due to channeling effects and the impossibility of reaching equilibrium at such a high flow-rate. Therefore an optimization must be made to find the optimum value for the flow rate as a compromise to the amount of carbon dioxide used.

#### *Effect of Co solvent Modifiers on SCFE*

Supercritical CO<sub>2</sub> has good solvent properties and is often used for extraction of non-polar compounds and some polar compounds. Sometimes the extraction must be carried out without modifier as in the case of extraction of Vitamin E and provitamin A being lipophilic compounds, supercritical carbondioxide is considered a relatively good solvent for extraction. Pure CO<sub>2</sub> is not widely used for the extraction of hydrophilic compounds and a common practice in SCFE is to change the polarity of the supercritical fluid by addition of small amounts of organic co-solvents and thereby increasing the solvating power towards the target compounds. The cosolvents interact strongly with analytes (hydrogen-bonding, dipole-dipole and others polarity interactions) which results in significant improvement the extraction yields. Most commonly used co- solvents in SCFE are ethanol and methanol. There are two main procedures by which co-solvents or modifiers can be incorporated in the SCFE process; mixing of the modifier with the CO<sub>2</sub> flow and mixing the modifier with raw material in the extraction cell. In a work done by Benelli et al., the use of ethanol as co-solvent with CO<sub>2</sub> increased the extraction yield of orange pomace extracts by rupturing the solute/solid matrix interactions, and substituting co-solvent molecules in solid active sites. Adil et al. also studied that ethanol concentration increased the total phenolic content of the extracts from peach pomace due to increased phenol-alcohol interactions and thus increasing the solvating power of CO<sub>2</sub>. In addition, ethanol increases the bulk density of SC-CO<sub>2</sub> due to the higher density of the co-solvent and clustering of SC-CO<sub>2</sub> molecules around the cosolvent. However, in a work done by Lamin et al., recovery of lycopene increased in the higher temperature regions where the ethanol concentration was low but higher temperature had a detrimental effect on lycopene as a result of instantaneous heating. Temperature dependence to solubility enhancement was reported by Vega et al., they also illustrated higher ethanol

concentration to be less effective as the temperature increases. This phenomenon was also proven by Baysal et al. with a higher recovery at 5% modifier concentration compared to 10% at a temperature of 40 °C.

#### *Effect of Feed Composition on SCFE*

According to Louli et al., composition of the feed had the most significant effect on the extract's antioxidant activity. In case of red grape pomace free of stems, a much more active extract was obtained due to the less inactive compounds extracted during the initial extraction which resulted in increased antioxidant activity of the extract after its SCF treatment.

In a work done by Nobre et al., two samples of tomato industrial waste, with different trans-lycopene content, were submitted to SCFE at 60°C and 300 bar. It was reported when the feed had a lower content of trans-lycopene the recovery was faster and higher. In addition, when the starting material had a higher content of trans-lycopene, the solvent/feed ratio increased i.e. the amount of CO<sub>2</sub> required for the extraction was higher for the same flow-rate, and increase in the extraction time resulted in degradation of the trans-lycopene in the extraction cell, thus lowering the recovery of trans lycopene.

#### *Effect of Moisture Content on SCFE*

The moisture content of the feed plays an important role during the extraction of bioactive compounds. The extraction yield of  $\beta$ -carotene increased from 15 to 72 $\mu$ g/g dry pomace as moisture content of feed decreased from 14 to 10% 9 (w/w). It was concluded that high moisture content was a hindrance to CO<sub>2</sub> diffusion into the pores; also, it made the apricot pomace sticky, which reduced CO<sub>2</sub>-sample contact. Nobre et al. reported similar results that the yield of trans-lycopene was higher and faster from tomato waste with lower moisture content, although the drying of feed to reduce moisture (4.6%) led to a significant decrease in its trans-lycopene content.

#### *Effect of Pretreatment on SCFE*

Differences in the quality have been observed between the extracts obtained from samples of different origins and samples stored at air-dried and frozen conditions. For maximum recovery of high valued products, the by-products must be stored at frozen condition rather than air-dried state. Presence of water in plant tissue interferes with the effectiveness of SCFE by CO<sub>2</sub> as it

hinders the diffusion of the SC-CO<sub>2</sub> into the solid matrix. Thus, different techniques such as oven-drying, freeze-drying or using adsorbents have been investigated for removing water from the sample. It has been reported that the extraction yield of freeze-dried samples was higher than that of oven-dried samples.

In a work done by Louli et al., the effect of feed pretreatment (crushing) on the super critical extraction of the antioxidants from red grapes pomace was investigated and it was reported that crushing the pomace resulted in a small increase of the extracted phenols. Crushing was therefore not considered as a decisive parameter for increasing the efficiency of the process.

According to Mukhopadhyay and Karamta, pretreatment of washing the ground feed with water-soluble organic solvent and subsequent extraction with same solvent facilitated the easy removal of bound water to get dehydrated feed and also resulted in enrichment by removal of undesirable constituents from the dehydrated feed. The lycopene content in the extract as extracted by solvent extraction improved from 2.7% (from dehydrated feed) to 4.5% (from enriched feed). SCFE cum-fractionation from such enriched feed resulted in efficient recovery of active ingredients with high purity within 2-5 h at 300-450 bar and 60-70°C.

In a work done by Claudia et al., the SCFE of grape seed oil using CO<sub>2</sub> was performed isothermally at 313.15K, and at 160, 180, and 200 bar, using both untreated and enzymatically pre-treated seed. The pre-treatment was carried out with cell wall degrading enzyme (mixture of cellulase, protease, xylanase and pectinase). The maximum extraction yield for untreated seed obtained was 11.5%, whereas the enzymatic pre-treatment of the seed increased the yield by 43.5%.

## Fundamentals of Mass Transfer and Phase Equilibria Relating To Supercritical Fluid Extraction

### *Thermodynamic Description of Phase Equilibrium with Supercritical Fluids*

A system is considered to be at equilibrium when there is no change in pressure, temperature and compositions in each phase. Phase equilibria of mixtures are of particular importance in order to define system properties. There are several types of

phase equilibria that include liquid-liquid, liquid-vapor, liquid-liquid-vapor, liquid-solid-vapor, solid-liquid, solid-liquid-liquid and solid-vapor. The calculations of solid-fluid equilibrium at high pressure are important in the modeling and design of processes that use supercritical fluids to extract solid solutes.

### 1) Solid Solubilities

The solubility of the solids in the gas phase of the supercritical fluid can be obtained using the following correlation (equation1) assuming the solid is a pure component:

$$y_2 = E \frac{p_2^s}{P} \quad (1)$$

where E is the enhancement factor over ideal solubility

$p_2^s$  is the sublimation pressure of the solute

For a low-volatility, incompressible solid solute, the enhancement factor can be calculated as (equation2) :

$$E = \frac{\exp\left(\frac{(P-p_2^s)v_2^{sol}}{RT}\right)}{\phi_2} \quad (2)$$

where  $\phi_2$  is the fugacity coefficient of the solid solute in the gas phase.

$v_2^{sol}$  is the solid molar volume.

At the supercritical region, the distinction between the liquid and gas states begins to disappear as supercritical fluids display characteristics of both. Therefore supercritical fluids can be modeled as either expanded liquids or compressed gases. Modeling supercritical fluids as compressed gases is very similar to the liquid model. For the compressed gas model, following assumptions are made: vapor pressure is small, molar volume of the solute is pressure independent, the fugacity coefficient of the solute at saturation is unity, so the fraction of solid dissolved is given by:

$$y_2 = \frac{p_2^s \exp\left(\frac{v_2^s P}{RT}\right)}{\phi_2} \quad (3)$$

where,  $y_2$  is mole fraction of solute in supercritical phase.

P is the solid's vapor pressure

V is the solid's molar volume

$\phi_2$  is the solid's fugacity coefficient in the supercritical fluid phase

R is universal gas constant

The saturation or the sublimation pressure ( $p_2^s$ ) can be referred from literature or calculated by:



$$\log p^{sat} = A - \frac{B}{T(K)+C} \quad (4)$$

where A, B, and C are the Antoine equation constants.

## 2) Equations of State

Thermodynamic modeling employs equations of state (EoS) which are an important tool for the correlation and prediction of thermodynamic properties and phase behavior of pure substances. Cubic equations of state are a group of equations obtained by modifying the Van der Waals equation of state and are used to calculate thermophysical properties and phase equilibria. This approach proves to be simple and the most widely used in analyzing experimental data. In the present work, the Peng Robinson equation of state (PR-EoS), Redlich-Kwong (RK) and Soave-Redlich-Kwong (SRK), and were chosen to model the high-pressure phase behavior that are developed first for pure component, and then extended to mixtures through the use of mixing rules for combining the pure component parameters.

### 1) Peng-robinson Equation of State

The Peng-Robinson (PR) equation of state was developed in 1976 and is the most popular cubic equation of state. The equation focuses on several important factors that include having parameters modeled in terms of critical temperature and pressure as well as the acentric factor. The equation aims at better approximating liquid densities and compressibility factors, Z<sub>c</sub>. The basic form of the equation is given by:

$$P = \frac{RT}{V-b} - \frac{a(T)}{v^2 + 2bv - b^2} \quad (5)$$

Where a and b are given at the critical temperatures and pressures by:

$$a(T_c) = \frac{0.4572 R^2 T_c^2}{P_c}, \quad b(T_c) = \frac{0.07780 R T_c}{P_c}$$

$$T = [1 + m(1 - T_r^{1/2})]^2$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

For mixtures, the PR parameters are obtained using the mixing rule of Van der Waals. The energy parameter, a, is given by (equation 6):

$$a = \sum \sum y_i y_j a_{ij} \quad (6)$$

Where the cross parameter, a<sub>ij</sub>, is given by the combination rule:

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (7)$$

The volume parameter, b, is calculated from:

$$b = \sum y_i b_i \quad (8)$$

Where, a<sub>i</sub> and b<sub>i</sub> are pure component parameters, x<sub>i</sub> mole fraction of component i and k<sub>ij</sub> is binary interaction parameter.

### 2) Redlich-Kwong EOS:

The Redlich-Kwong equation of state can be written in the following form (equation 9):

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}(v-b)} \quad (9)$$

The Van der Waals mixing rules for the Redlich-Kwong equation of state will be in the following form (equation 10 & 11):

$$a = \left\{ \sum_i^n \sum_j^n x_i x_j a_{ij}^{2/3} b_{ij}^{1/3} \right\}^{1.5} / \left( \sum_i^n \sum_j^n x_i x_j b_{ij} \right)^{1/2} \quad (10)$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij} \quad (11)$$

$$\text{So, } b = 0.08664 \frac{RT_c}{P_c}, \quad a = 0.42747 \frac{R^2 T_c^2}{P_c}, \quad \alpha(T) = T_r^{-1/2}$$

### 3) Soave-redlich-Kwong EoS :

In 1972 G. Soave replaced the 1/√(T) term of the Redlich-Kwong equation with a function α(T,ω) involving the temperature and the acentric factor (the resulting equation is also known as the Soave-Redlich-Kwong equation). The SRK equation can be written in a general form as follows (equation 12):

$$P = \frac{RT}{V-b} + \frac{a_c \alpha(T_r)}{V(V+b)} \quad (12)$$

The parameters a and b for pure substances are determined using the critical properties and the acentric factor. For mixtures, the parameters a and b are concentration dependent. Here,

$$\alpha = [1 + m(1 + T_r^{1/2})]^2 \quad (13)$$

$$m = 0.48 + 1.57\omega - 0.176\omega^2 \quad (14)$$

$$T_r = \frac{T}{T_c} \quad (15)$$

Where, ω is acentric factor.

## 3) Empirical Equations for Phase Equilibria Calculations

### 1) Chrastil's Model (CH)

The Chrastil's model is based on the formation of a solvation complex between the solvent and the solute molecules in equilibrium, showing a linear relation between solubility, solvent density and process temperature (equation 16):

$$\ln y^* = k \ln \rho + \frac{a}{T} + b \quad (16)$$

where  $a$ ,  $b$  and  $k$  represent the adjustable constants of the model in which 'a' depends on the heat of solvation of solute and association constant 'k' indicate the average number of CO<sub>2</sub> molecules present in the complex solute-solvent,  $y^*$  represents the solute solubility (g/L),  $T$  is the temperature (K) and  $\rho$  is the solvent density (g/L). The  $a$  and  $b$  parameters are vaporizing enthalpy and molecular weight dependants, respectively. The Chrastil equation has the advantage of having only three parameters to fit the experimental data.

### 2) Del Valle & Aguilera's (DVA) Model

The del Valle and Aguilera model is a modification of the Chrastil's model and the changes are based on the behavior of solubility data from several vegetable oils, such as corn, soy and sunflower. The proposed equation is adequate for a temperature range from 293 to 353 K and for pressure varying from 150 to 880 bar (equation 17):

$$\ln y^* = k \cdot \ln \rho + \frac{a}{T} + b + c \quad (17)$$

where  $c$  is constant.

### 3) Enhancement Factor's Model (EF)

This model considers a linear relation between enhancement factor ( $E$ ) and solvent density and relates the solute solubility with  $E$  and the solute vapor pressure, as shown in the following equations (18) and (19):

$$\ln E = A + B\rho \quad (18)$$

$$y^* = \frac{P^s}{P} \cdot E \quad (19)$$

where  $E$  is the enhancement factor,  $\rho$  is the density of CO<sub>2</sub> (g/L),  $A$  and  $B$  the adjustable model parameters,  $y^*$  is the solubility (kg oil/kg CO<sub>2</sub>),  $P^s$  is the solute vapor pressure (bars) and  $P$  the system pressure (bar). The enhancement factor model is very useful for data correlation because of its simplicity and good fits.

Equations of state can be used over wide range of temperature and pressure, and they can be applied to mixtures of distinct components, ranging from the light gases to heavy liquids. Even if good results have been obtained, cubic equations of state are known to be inadequate for the proper description of the critical region. The Peng-Robinson and Soave-Redlich-Kwong equations are used widely in industry. The advantages of these

equations are that they can accurately exhibit the relation among temperature, pressure, and phase compositions in binary and multicomponent systems as they only require the thermodynamic properties and acentric factor for the generalized parameters. Little computer time is required and good phase equilibrium correlations can be obtained. Chrastil's equation take into account the effect of temperature and solvent density on solute solubility has found many applications in modeling the extraction from solid matrices. The advantage of using the Chrastil equation is the model does not require any physical chemical property data of the solute. But Chrastil's equation is not valid over a wide range of temperature and because of this limitation, several modified forms have been developed and Del Valle–Aguilera equation better accounts for temperature effects as it has only one more adjustable parameter.

## Mathematical Modeling of SCFE Based On Mass Transfer Approaches

The optimization of operational parameters used in SCFE is of great importance for making this technique economical, as the investment cost is relatively high. For the prediction of the viability of SCFE processes on an industrial scale, it is possible to determine parameters for process design as equipment dimensions, solvent flow rate, and particle size through the simulation of overall extraction curves by using an accurate mathematical description of the extraction process and experimental laboratory data. Different types of mathematical models have been reported in literature for describing the SCFE process. These include theoretical, semi-empirical and empirical models. Almost every model in the literature considers the extract as a pure substance, although it may contain several components of different chemical characteristics. The models used to correlate experimental results from SCFE can be classified as:

- (i) empirical models
- (ii) models based on Fick's second law of diffusion
- (iii) models based on differential mass balances along the extraction bed

### 1) Mathematical Models Based in Empirical Analysis

According to Esquivel et al. the extraction curves can be evaluated by an empirical model. A simple

empirical equation was applied to fit the extraction curves representing the extraction yield against time of extraction in terms of a Langmuir-like-empirical equation.

$$e = e_{\text{lim}} \left( \frac{t}{t+b} \right) \quad (20)$$

where  $e$  is the ratio of the mass of oil recovered in time  $t$  (s) to the initial mass of solute-free feed, (kilograms of oil per kilogram of solute-free feed) and  $e_{\text{lim}}$  is the maximum yield after infinite extraction time,  $e_{\text{lim}}/b$  is the initial slope of specific oil yield as a function of time. Value of  $b$  can be determined by linearization of the equation (20):

$$\frac{1}{e} = \left( \frac{b}{e_{\text{lim}}} \right) \frac{1}{t} + \frac{1}{e_{\text{lim}}} \quad (21)$$

Limitation of equation (20) is that it doesn't include interactions between solute and solid matrix and data regarding oil fractionation during extraction process cannot be obtained.

Comim et al. concluded in their work from the SCFE of dried banana peel, the application of Esquivel model only required the raw material extraction rate (kg/kg) value and the raw material mass used, for this reason it is a model of easy implementation. The fact that this model demonstrates only one adjustable parameter,  $b$ , it does not give information about the different types of mass transfer mechanisms. This fact has been further verified by Benelli et al. in their work on supercritical extraction from orange pomace and reported that the Esquivel model had the poorest fitting with a  $b$  value of 70.8716, probably because this model is based on heat analogy and not on mass transfer phenomenon.

## 2) Mathematical Models Based on Fick's Second Law of Diffusion:

Supercritical extraction is a diffusion-based process, with the solvent required to diffuse into the matrix, and the extracted material to diffuse out of the matrix into the solvent. Fick's law, states that flux is proportional to concentration gradient and diffusion of a compound occurs in the direction of decreasing concentration.

### Single Sphere Model

Subra et al. and Esquivel et al. applied single sphere model to  $\beta$ -carotene and olive oil extraction respectively. In this model, assumptions were made

that the solute is extracted from a solid matrix, which is composed of porous inert spheres of same size. All particles are at the same stage of extraction and extraction takes place by process similar to diffusion, which is governed by Fick's law. By analogy with the problem of immersion of a hot sphere into a cold fluid, the ratio of the mass,  $m_t$ , of extractable material that remains in the matrix after extraction for time  $t$  to that of initial mass of extractable material,  $m_0$ , can be expressed as:

$$\frac{m_t}{m_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{r^2}\right) \quad (22)$$

where  $n$  is an integer and  $D$  is the effective diffusion coefficient of the material ( $\text{m}^2/\text{s}$ ) in the sphere of radius  $r$  ( $\mu\text{m}$ ).

However, in work done by Comim et al. and Benelli et al. this model gave poorest fit as it considered the extraction process is controlled only by diffusion. Model presented the highest MSE values, probably because the convection mechanism was not considered. Subra et al. concluded that large sized carrot particles are not spherical so the extraction curves didn't provide an intercept of  $\ln(6/\pi^2)$ . Therefore, they treated the data according to the single stage diffusion (equation 22a) and two stages diffusion mechanisms (equation 23).

$$\frac{C-C_{\infty}}{C_{\infty}} = \exp(-kt) \quad (22a)$$

$$\frac{C-C_{\infty}}{C_{\infty}} = f_1 \exp(-k_1 t) + f_2 \exp(-k_2 t) \quad (23)$$

where  $C$  is the concentration of extracted solute at time  $t$  ( $\text{kg}/\text{m}^3$ ) and  $C_{\infty}$  is concentration at infinite time ( $\text{kg}/\text{m}^3$ ),  $f_1$  is the fraction of solute which is extracted with a rate constant  $k_1$ ; and  $f_2$  is the fraction extracted with rate constant  $k_2$ .

Esquivel et al. concluded that the model gave a good fit to the experimentally determined yield versus time data for 313 K at the highest superficial velocities studied but the results were not acceptable at the lowest velocities. The implications of allowing rapid equilibration to occur between the pore fluid and adjacent adsorbed solute are discussed and are in line with the fitted values of  $De$  and the behavior of the 'best fit' curves.

## 3) Models Based on Differential Mass Balances Along the Extraction Bed

### 1) Differential Mass Balance Model

The assumptions made in this model are:

1. The matrix is a porous solid where extract is uniformly distributed throughout the particles.
2. The system is isothermal
3. The radial concentration gradients through the bed are neglected
4. The axial dispersion is accounted
5. The fluid physical properties are constant
6. The matrix is approximated by spherical particles with uniform structure and radius.
7. The bed structure remains constant.

The governing equations in continuous flow extractor are:

$$\frac{\partial C_f}{\partial t} + \frac{v}{\epsilon} \frac{\partial C_f}{\partial z} = \frac{1-\epsilon}{\epsilon} a_s k_f (C_{p/r=R} - C_f) + \frac{D_f}{\epsilon} \frac{\partial^2 C_f}{\partial z^2} \quad (24)$$

$$\epsilon_p \frac{\partial C_p}{\partial t} = D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_p}{\partial r} \right) - \mathfrak{N} \quad (25)$$

$$\frac{\partial C_s}{\partial t} = \mathfrak{N} \quad (26)$$

The local dissolving rate  $\mathfrak{N}$  was further assumed to be described by an irreversible dissolution (equation 27):

$$\mathfrak{N} = -k_d C_s \quad (27)$$

where  $D_f$  is axial dispersion coefficient (m<sup>2</sup>/s),  $D_p$  is the intraparticle effective diffusivity (m<sup>2</sup>/s),  $k_f$  is external mass transfer coefficient (m/s) and  $k_d$  is the desorption rate constant (per sec),  $C_p$  is concentration of solute in the SCF (kg/m<sup>3</sup>),  $C_p$  is concentration of dissolved solute in the fluid phase within the substrate pores (kg/m<sup>3</sup>).

## 2) Extended Lack's Plug Flow Model

Sovova and Equivsel et al. extended Lack's plug flow model for application to SFE in case of ruptured cells or at the outer surfaces of particles where some of the solute is easily accessible to the solvent while rest of the solute present in deep pore structure is less accessible. While applying the model, assumptions are made that temperature and pressure are constant during extraction, solid bed is homogeneous with respect to particle size, distribution of solute and solvent is axially through a bed of milled particles and at the extractor inlet solvent is solute free. According to this model there are three extraction periods i.e. the initial period (extraction is at constant rate), transition

period (readily accessible oil is removed), and last period (solute deep inside is removed). One disadvantage of this model is greater number of experimental determinations for the validation of five model parameters  $Z$ ,  $w$ ,  $y_r$ ,  $x_0$  and  $x_k$ .

$$e = \begin{cases} qv_r [1 - \exp(-Z)] & q < q_m \\ y_r [q - q_m \exp(z_w - Z)] & q_m \leq q < q_n \\ x_0 - (y_r / W) \ln \{1 + [\exp(Wx_0 / y_r) - 1] \exp[W(q_m - q)x_k / x_0]\} & q \geq q_n \end{cases} \quad (28)$$

$$Z = \frac{k_f a_0 \rho}{(1-\epsilon) q \rho_s} \quad (29)$$

$$W = \frac{k_s a_0}{q(1-\epsilon)} \quad (30)$$

$$q_m = \frac{x_0 - x_k}{y_r Z} \quad (31)$$

$$q_n = q_m + \frac{1}{W} \ln \left[ \frac{x_k + (x_0 - x_k) \exp(Wx_0 / y_r)}{x_0} \right] \quad (32)$$

$$Z_w = Z \frac{y_r}{W x_0} \ln \left\{ x_0 \exp \left[ \frac{W(q - q_m) - x_k}{x_0 - x_k} \right] \right\} \quad (33)$$

where  $e$  is the amount of extract (kg/kg, extract/solute free feed),  $q$  is the dimensionless amount of solvent consumed (kg/kg, extract/solute free feed),  $q_m$  is the  $q$  value when extraction begins inside the particles i.e. when the transition period begins,  $y_r$  is the apparent solubility (kg/kg, extract/solvent),  $x_0$  is the solute concentration inside the particles (kg/kg, solute/solute free feed),  $Z$  and  $W$  are dimensionless parameters proportional to the solvent and solid mass transfer coefficients respectively,  $k_s$  is the solid mass transfer coefficient (m/s),  $a_0$  is the specific interfacial area (m<sup>2</sup>/m<sup>3</sup>),  $\rho_s$  and  $\rho$  are the solid and solvent densities (kg/m<sup>3</sup>) and,  $\epsilon$  is the bed porosity and  $q$  is the specific flow rate of the solvent (kg/kg/s, solvent/solute free feed).

Parameters  $Z$ ,  $W$ ,  $y_r$ ,  $x_0$  and  $x_k$  were calculated by matching the calculated and the experimental data using a Nelder-Mead technique to minimize the objective function based on time versus the amount of extract collected. The value of  $Z$  for the initial period was calculated using the solvent film mass transfer coefficient and experimentally measured values for the bed voidage  $\epsilon$  (0.60 for batch I and 0.57 for batch II),  $a_0$  was calculated using  $a_0 = 6(1 - \epsilon) / \text{particle diameter}$ .

In a work done by Mira et al., the kinetic extraction of the essential oil from orange peel was done using the Lack's plug-flow model and gave excellent results as the standard deviations between experimental data and calculated values were very small in all experiments. Mass transfer coefficients decreased on increasing particle size of orange peel

and the parameter  $Zq$  increased on increasing  $\text{CO}_2$  mass flow but on reaching a fixed value, it remained constant. In a work done by Berna et al., the influence of the height of the particle bed on the kinetics of supercritical fluid extraction (SFE) of essential oil from peels of dehydrated oranges of two different cultivars was done. The results of the experiments were interpreted using Sovova's extended flow model and reported that the difference in the value of the mass transfer coefficient of the solid phase ( $W_q$ ) may be associated with the differing oil content of the raw material and its differing distribution. When the weight of the fraction of difficult-access solute ( $x_k$ ) increases and the particle size is same, the transfer will be easier, and the mass transfer coefficient increases because solute is closer to the surface. The differences in the values of the mass transfer coefficient for the fluid phase ( $Z_q$ ) are more difficult to explain because this parameter is influenced by flow rate, height of the particle bed and particle diameter.

### 3) Shrinking Core Model

This model describes the situation of the irreversible desorption followed by diffusion in the porous solid through the pores. When the mass-transfer rate of the solute in the non-extracted inner part is much slower than that in the outer part where most of the solute has been extracted, or the solute concentration is much higher than the solubility of the solute in the solvent phase, a sharp boundary may exist between the outer and inner regions. A core of the inner region shrinks with the progress of the extraction.

The shrinking core model assumes that there is a sharp boundary between the extracted and non-extracted parts of the particle. As extraction proceeds, the boundary recedes until it reaches the center of the particle and all solute is exhausted. In the development of the mass balances to the core and extracted phases, it is assumed that there is no solute accumulation in the extracted region and the solute diffuses from the boundary to the surface through the pore network. Therefore, all solute leaving the particle by convection at surface comes from the core. The mass balances to the core and to the extracted phases of a spherical particle are given. Bhupesh et al. applied shrinking core model in the SCFE of ginger oil and found that the model gave a good fit for large sized particles, but in the

case of smaller particle sizes, only the initial part was satisfactorily described. In the case of smaller particle sizes, particles of ginger root were not spherical and tended to agglomerate, resulting in channeling in the bed and nonhomogeneous distribution of the solute in the bed within the extractor. So it was concluded in their study that the shrinking core model may not be suitable for smaller particle sizes where the cell size was almost the same as the particle size.

According to Doker et al., in the modeling of extraction of  $\beta$ -carotene from apricot bagasse using supercritical  $\text{CO}_2$ , shrinking core model was selected as the best mathematical model as it characterized the extraction process after taking into consideration the mass transfer mechanisms such as adsorption, diffusion, solubility, and desorption. The following assumptions were made to derive fundamental equations:

1. The process is isothermal and isobaric
2. The matrix is a porous material where the extract is uniformly distributed throughout the particle
3. The physical properties of the supercritical fluid are constant during the extraction and flows axially with an interstitial velocity  $v$  through a packed bed in a cylindrical extractor of height  $L$
4. Radial dispersion is neglected, axial dispersion considered
5. Extraction is irreversible desorption.

Considering axial dispersion, the material balance on the bulk fluid phase in the extractor is:

$$\frac{\partial C}{\partial t} + V \frac{\partial C}{\partial z} = D_L \frac{\partial^2 C}{\partial z^2} - \frac{1-\epsilon}{\epsilon} \frac{3k_f}{R} (C - C_i(R)) \quad (34)$$

Temporal variation of solid phase concentration (average oil concentration in a particle) is equated with the rate of mass transfer of the solute within the external film surrounding the particle.

$$\frac{\partial q}{\partial t} = \frac{3k_f}{R} (C - C_i(R)) \quad (35)$$

The diffusion in the outer region is given by

$$\frac{D_e}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_i}{\partial r} \right) = 0 \quad (36)$$

Solid phase solute exists within the core

$$\frac{q}{q_0} = \left( \frac{r_c}{R} \right)^3 \quad (37)$$

Boundary conditions are given as follows. At the core boundary the concentration in the fluid phase is at its saturation value.

$$C_i = C_{sat} \quad \text{at } r = r_c$$

Diffusion flux at the outer surface of the particle is equal to the mass transfer through the external film.

$$\left(D_e \frac{\partial C_i}{\partial r}\right)_{r=R} = k_f(C - C_i(R)) \quad (38)$$

Initial conditions are given as follows.

$$\left. \begin{aligned} vC - D_L \frac{\partial C}{\partial z} &= 0 \text{ at } z = 0 \\ \frac{\partial C}{\partial z} &= 0 \text{ at } z = L \\ C &= 0 \text{ at } t = 0 \\ C_i &= C_{i,0} \text{ at } t = 0 \\ r_c &= R \text{ at } t = 0 \end{aligned} \right\} \quad (39)$$

The following dimensionless groups are defined to derive dimensionless formulas of the fundamental equations.

$$\left. \begin{aligned} x &= C/C_{sat} & x_1 &= C_1/C_{sat} & x_0 &= C_{1,0}/C_{sat} \\ \xi &= r/R & Z &= z/L & a &= vR^2/D_e L \\ \theta &= (D_e/R^2)t\bar{y} = \bar{q}/q_0 b = C_{sat}/q_0 \\ Bi &= k_f R/D_e & Pe &= Lv/D_L \end{aligned} \right\} \quad (40)$$

Variations of dimensionless concentration and dimensionless core radius are expressed as:

$$\frac{\partial x}{\partial \theta} + a \frac{\partial x}{\partial Z} = \frac{a}{Pe} \frac{\partial^2 x}{\partial Z^2} - \frac{1-\epsilon}{\epsilon} \frac{3Bi(x-1)}{1-Bi(1-1/\xi_c)} \quad (41)$$

$$\frac{\partial \xi_c}{\partial \theta} = \frac{bBi(x-1)}{\xi_c^2 [1-Bi(1-1/\xi_c)]} \quad (42)$$

$$\bar{y} = \xi_c^3 \quad (43)$$

Boundary and initial conditions are:

$$\left. \begin{aligned} x - \frac{1}{Pe} \frac{\partial x}{\partial Z^2} &= 0 \text{ at } Z = 0 \\ \frac{\partial x}{\partial Z} &= 0 \text{ at } Z = 1 \\ x &= 0 \text{ at } \theta = 0 \\ x_i &= x_0 \text{ at } \theta = 0 \\ \xi_c &= 1 \text{ at } \theta = 0 \end{aligned} \right\} \quad (44)$$

Equations (41), (42) and (43) along with their respective initial and boundary conditions can be solved numerically using a fourth order Runge-Kutta method or by Crank Nicholson's method.

#### 4) Simple Single Plate Model (SSP model)

The Simple single plate model assumes: uniform distribution of oil within the plate like particles, particles are at the same stage of extraction, intraparticle diffusion, concentration in the fluid phase is negligible, stagnant film's resistance to mass transfer is negligible and the mass extracted from the bed equals that extracted from the particles (fluid phase mass balance is neglected).

The SSP model equation can be expressed as:

$$E(t) = E_\infty \left[ 1 - \sum_{n=1}^{\infty} \frac{8}{(2n+1)^2} e^{(-D_m(2n+1)^2 \pi^2 t)/\delta^2} \right] \quad (45)$$

where  $E(t)$  and  $E_\infty$  are the extraction degree (%) after time  $t$  and infinite,  $D_m$  is the matrix diffusivity ( $m^2/s$ ),  $\delta$  is the thickness of particles ( $m$ ) or plates and  $n$  is an integer.

In a work done by Benelli et al. the curve modeling for orange pomace extract was performed using SSP model and reported the highest MSE values (0.0011) probably because the convection mechanism was not considered.

#### 5) Single Plate Model (SP)

The SP model was derived from the equations given by Wong for the heat loss from an infinite slab to a surrounding medium that were translated to mass transfer context using the heat-mass transfer analogies. It is based on the same assumptions as the SSP model except in the allowance for an external resistance. The model equation is given below,

$$E(t) = E_\infty \left\{ 4 \sum_{n=1}^{\infty} \frac{\sin^2 \beta_n}{2\beta_n^2 + \beta_n \sin 2\beta_n} \times \left[ 1 - e^{-(2\beta_n/\delta)^2 D_m t} \right] \right\} \quad (46)$$

$$\beta_n \tan \beta_n = \frac{k_f \delta}{2D_m} \quad (47)$$

where  $k_f$  is the film coefficient and  $\beta_n$  are the positive roots of the implicit equation.

#### 6) Fluid Phase/Simple Single Plate Model (FP/SSP)

According to the Fluid Phase/Simple Single Plate model (equation 48), a fraction of essential oils are also present in the fluid phase at the start of the dynamic extraction. The intraparticle transport is same as described by the SSP model and axial dispersion; fluid phase density and porosity of the bed are constant along the bed and independent of the extraction time.

$$E(t) = \frac{M(t)}{M_{\infty}} = \frac{\int_0^t C(z=L,t) u_s A dt}{M_{\infty}} \quad (48)$$

Where,  $M(t)$  and  $M_{\infty}$  are the mass of oil extracted from the bed (kg) after time  $t$  and infinite,  $u_s$  is the superficial velocity of the solvent (m/s) and  $A$  the cross-sectional area of the bed ( $m^2$ ).

Gaspar et al. applied three models (SP, SSP and FP/SSP) to describe the extraction of essential oils from oregano bracts using compressed CO<sub>2</sub>. The first two models i.e. the Simple Single Plate and the Single Plate models, were based on the particle phase mass balance while the third model, the Fluid Phase/Simple Single Plate (FP/SSP), considered both particle mass balance and fluid phase mass balance. SSP and SP models include only one adjustable parameter i.e. the diffusivity of the essential oils within the matrix ( $D_m$ ), whereas in the FP/SSP model  $D_m$  and  $f_0$  (fraction of oil initially dissolved in the fluid phase) were both used as adjustable parameters.

According to Gaspar et al. (2003), all models gave a good fit to the experimental data while the FP/SSP model gave the best fit. The FP/SSP models presented consistently lower standard deviations than the SSP and SP models. It was concluded that despite of good fitting of these models to experimental data, the intraparticle transport of essential oils was difficult to predict which limits the ability of the models to predict extraction rates.

### 7) Logistic Model

According to Martinez et al. (2003), two phases exist in the extraction bed, the solid phase which is composed of the vegetable raw material from where the extract is obtained, and a fluid phase which is comprised of the supercritical solvent with the extract dissolved in it. The assumption made in this model is that both phases involved in the process are considered to occupy all of the volume of the extraction bed. The model is based on the mass balance of the extraction bed and neglects the accumulation and dispersion in the fluid phase because these phenomena have no significant influence on the process as compared to the effect of convection. The overall extraction curve (mass of extract,  $m_i$ ) can be represented by the following equation with only two adjustable parameters ( $b$ ,  $t_m$ ):

$$m_i(h = H, t) = \frac{m_{ti}}{\exp(b_i t_{mi})} \left\{ \frac{1 + \exp(b_i t_{mi})}{1 + \exp[b_i(t_{mi} - t)]} \right\} - 1 \quad (49)$$

Where  $m_{ti}$  is the total mass of single group of compounds (kg),  $H$  is the total length of the extraction bed (m),  $t_{mi}$  is the time of maximum extraction rate (min).

In their work of SCFE from dried banana peel by Comim et al. (2010), the logistic model presented the best adjustment to experimental data with lowest deviation and the negative values of  $t_m$  were obtained which suggested that the assays started with maximum extraction rate. Similar results were reported by Benelli et al. (2010) in their work of SCFE from orange pomace, the negative value of parameter  $t_m$  ( $t_m = -554.60$  min) indicated that the maximum rate is reached at the beginning of the extraction.

### Conclusion

SCFE has been suggested as the method of choice because it is a relatively rapid, inexpensive and reliable method for the extraction thermo labile compounds. The distribution of the natural materials within the solid structure affects the selection of the possible models. In this paper, a review of the relevant thermodynamic models employed for supercritical fluid extraction of solutes from liquids or solids is presented. To describe the time-dependent extraction curves, several approaches have been proposed in the literature which includes empirical, diffusion-based and differential mass balance models.

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